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CHANGES IN CHEMICAL QUALITY OF WATER USED FOR THE REMOVAL OF FLY ASH FROM POWER GENERATING STATIONS

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July. 1972

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Introduction:

Ontario Hydro proposes to utilize recycled water for the removal of fly ash collected by the precipitators from the coal-fired furnaces at its Nanticoke generating station. The collected fly ash will be slurried and transported by means of a water sluicing system to a settling lagoon. The fly ash will be removed by settling and the supernatant will be drawn off and recirculated. However, the lagoon will also receive an additional volume of service water from another source so that when it is filled, there will be a net input of water into the recirculation system. The volume of water involved is approximately 400 Igpm which must be discharged to Lake Erie in order to maintain a balance in the system.

Because of this, there is some concern about the levels of total dissolved solids (TDS) that may accumulate in the discharge water from the soluble materials leached from the fly ash. The build-up of TDS in the recirculating water may cause some impairment to the water quality and contaminate the water in Lake Erie.

It was the purpose of this study to conduct preliminary laboratory tests on samples of fly ash and examine the changes in chemical quality resulting in the water which has been subjected to mixing with several batches of fly ash.

Characteristics of Fly Ash

Fly ash is chiefly a product of combustion derived from the burning of pulverized coal in large industrial furnaces employed in the generating of steam. It is formed from the incombustible components in the coal and from some of the particles which have not been burned completely within the furnace proper. When examined microscopically, it may exhibit particles varying in shape and size. The average size may vary from less than one micron to approximately 80 microns. Its physical and chemical characteristics are determined by the type of coal used. Chemically, fly ashes produced from the majority of coals consist of alumina, silica, iron oxide, lime and magnesia with the percentage of any one constituent varying over a wide range of values depending on the sample of fly ash being analyzed.

Fly ash is removed from the smoke or flue gases and collected by means of mechanical or electrostatic precipitators. Since water will be used to remove and transport the fly ash from the precipitators at Nanticoke generating station, it is of interest to record some of the analytical data for fly ash samples reported in the literature.

TABLE I

Analysis of Fly Ash*

Component	Samples from			
	A	B	C	D
SiO_2 (%)	45.06	44.42	45.42	40.32
Fe_2O_3 (%)	15.60	12.62	11.54	13.39
FeO (%)	0.72	3.65	3.74	3.95
Al_2O_3 (%)	34.76	27.62	29.62	32.92
Ca (%)	0.37	3.10	1.93	2.34
Mg (%)	0.37	1.27	0.94	0.74
Carbon (%)	4.17	6.05	4.81	5.79
Specific Gravity	2.29	2.24	2.36	2.30

Experimental Details

For this study, samples of fly ash were obtained from Ontario Hydro's generating stations located at Lakeview, Lambton and Windsor. No special preparations were required for the samples from Lakeview and Windsor. Since the Lambton sample was found to be slightly moist at the time of arrival, it was air dried by spreading out on the laboratory bench for several days before any tests were conducted.

* Michael D. Nelson and Carmen F. Guarino
The Use of Fly Ash in Municipal Waste Treatment.
JWPCF 41 Part 1:1905-1911, No. 11 (1969)

The tests with the three samples of fly ash were all conducted essentially in a similar manner using tap water at the room temperature. Starting initially with a large volume of water (4-liters), 10 percent by weight of fly ash per measured volume of water was added and agitated vigorously for one hour, using a magnetic stirrer. After settling for at least one hour, the supernatant was decanted and analyzed for specific conductance, pH and total dissolved solids (TDS).

To simulate recycling, another portion of fly ash, 10 percent by weight was added to a measured volume of supernatant and mixed vigorously and the process was continued in the same manner as above. This procedure was repeated several times until the original volume was reduced to approximately one liter.

In an attempt to accelerate these tests, a series of tests were conducted with Lakeview fly ash using water heated and maintained at temperatures of 35 to 40 $^{\circ}$C during the mixing process.

Specific conductance and pH were the only analyses performed during the tests with the sample of fly ash from the Windsor station.

The final volume of supernatant from each series of tests was filtered and analyzed chemically for the presence of heavy metals and other constituents.

FIGURE 1

TESTS WITH FLY ASH FROM LAKEVIEW

GENERATING STATION

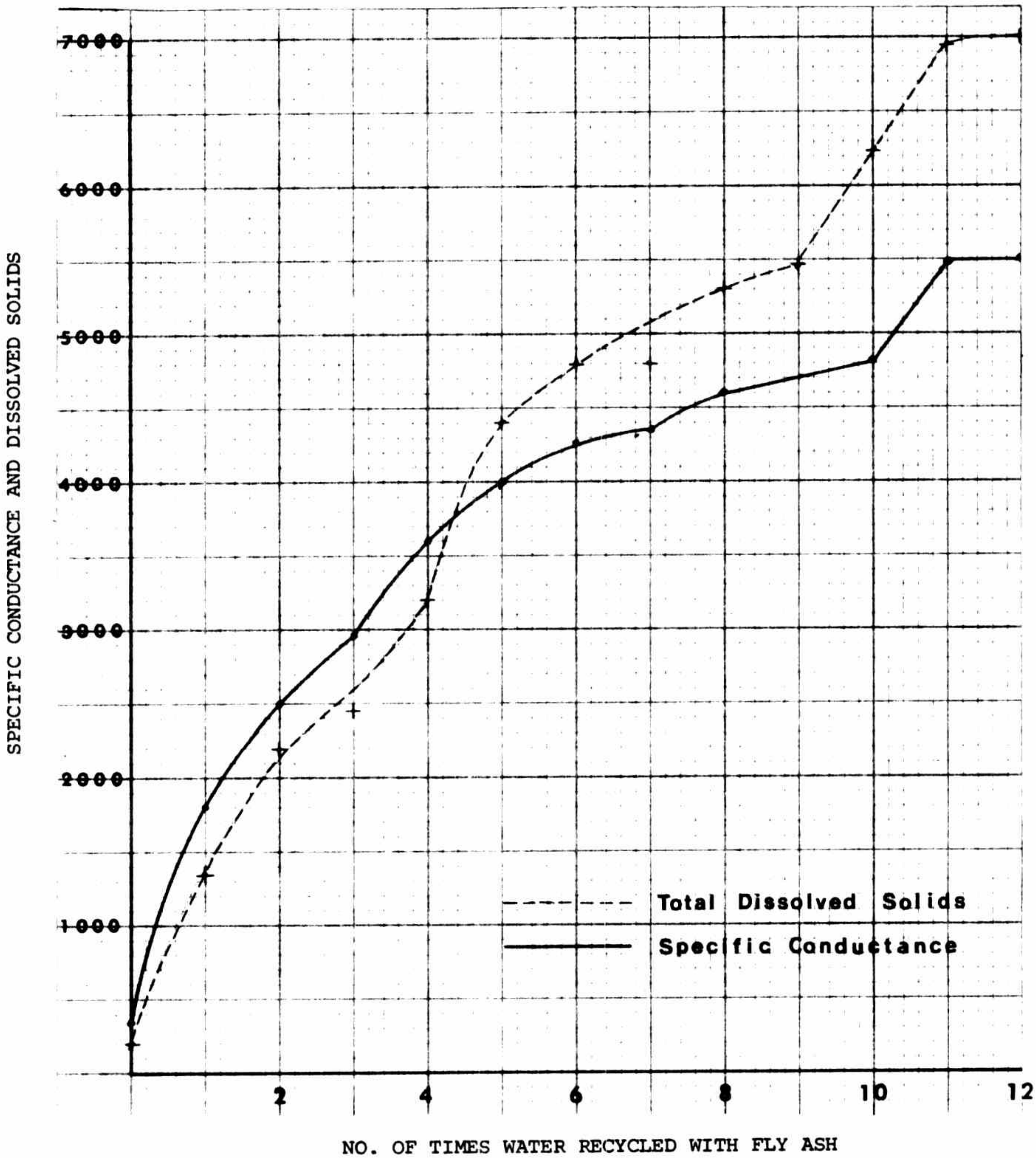
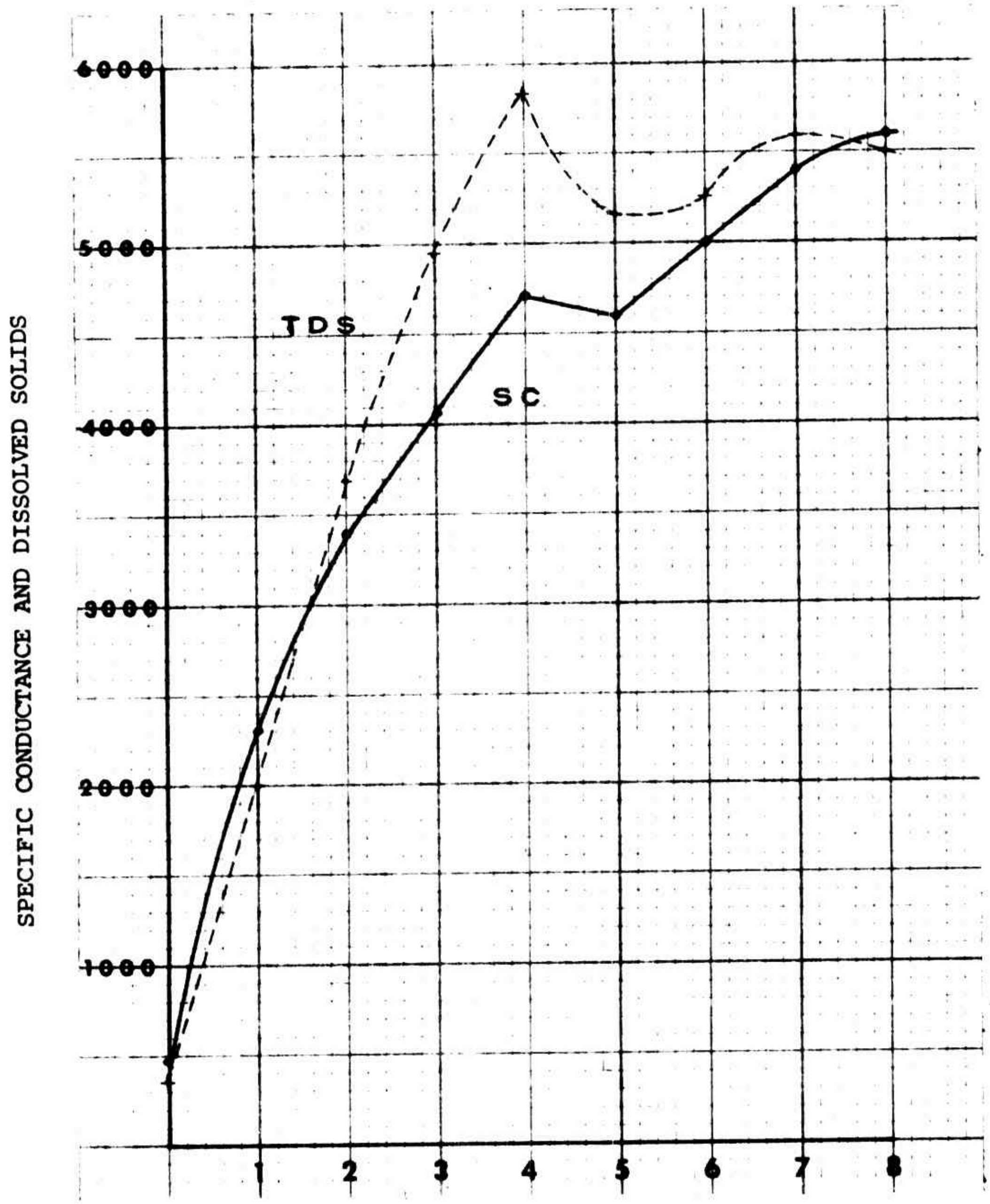


FIGURE 2

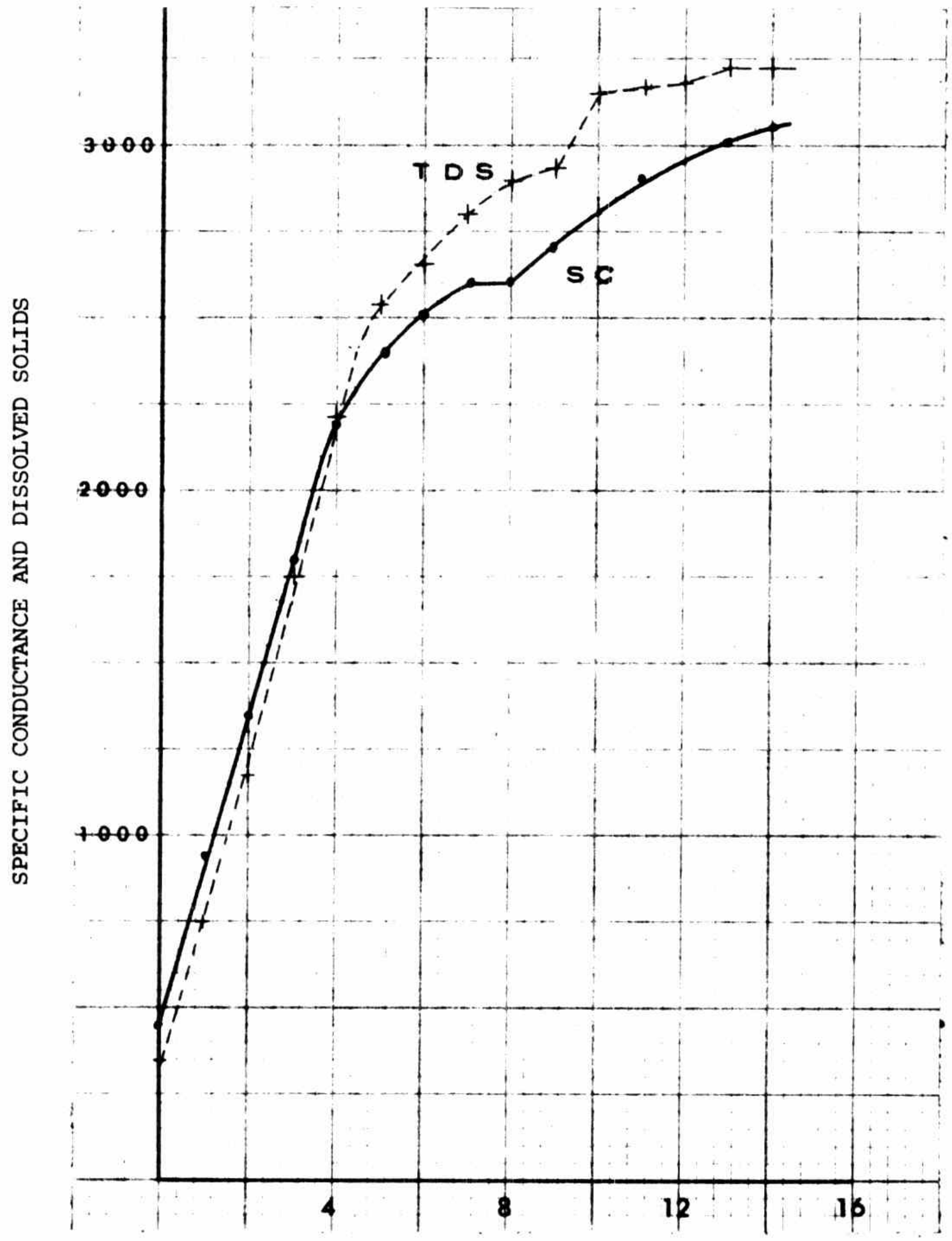
TESTS WITH FLY ASH FROM LAKEVIEW GENERATING STATION
IN WATER AT HIGHER TEMPERATURES



No. OF TIMES WATER RECYCLED WITH FLY ASH

FIGURE 3

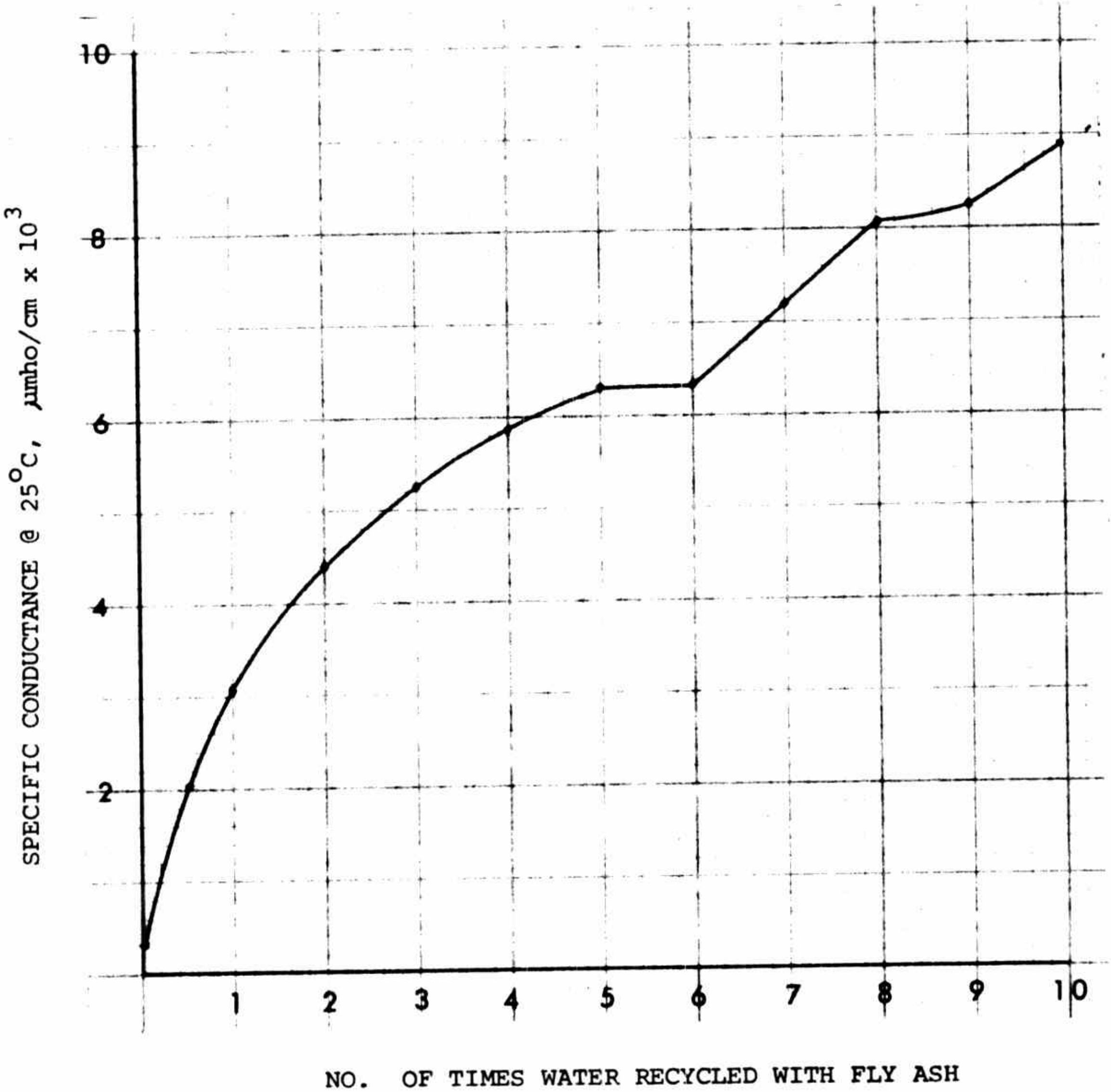
TESTS WITH FLY ASH FROM LAMBTON GENERATING STATION



NO. OF TIMES WATER RECYCLED WITH FLY ASH

FIGURE 4

TESTS WITH FLY ASH FROM J. CLARK KEITH GENERATING STATION



Discussion of Results:

Data related to TDS and specific conductance collected during each series of tests are presented graphically in Figures 1 to 4. They reflect the rise in TDS and the changes in the chemical quality taking place in the recirculating water after mixing with successive portions of fly ash.

The curves plotted from the data collected in the tests with Lakeview fly ash are depicted in Figures 1 and 2. Figure 1 shows the pattern of changes in TDS and specific conductance in the recirculating water at ambient temperatures of 23 to 25^{o}C while Figure 2 indicates the changes of the same parameters in the water at highest temperatures (35 to 40^{o}C).

In Figure 1, the curve depicting the changes in specific conductance shows a steady rise in the conductivity of the water then slight change at the 7th mixing and an effect of "levelling off" at the 11th mixing to a value of 6000 micromhos/cm. The TDS curve shows a steady rise to the 5th mixing, then a sharp rise and levelling off at the 7th mixing. It begins to rise again steadily and levelling off at 7000 mg/l in the 11th mixing. It should be noted that very fine white particles began to develop in the supernatant from the 7th and 8th mixings. The crystallization or the formation of the white precipitate became more pronounced in later samples especially if these were allowed to stand overnight. When these were agitated vigorously, a major portion of the precipitated materials redissolved.

Figure 2 shows curves of greater slopes indicating more rapid extraction of the chemical constituents taking place with the water at higher temperatures. A dip in the curve at the 5th mixing shows that there was a loss of TDS in the supernatant. The latter was allowed to stand overnight prior to the TDS analysis. In addition, the sample had copious amounts of precipitated material.

The curves in Figure 3 indicate that the amount of soluble materials released by the Lambton Fly Ash were generally at much lower levels than those from either of the other two samples of fly ash. The water in the tests with the Lambton sample was recycled with at least 14 different batches of fly ash. There was no immediate crystallization of the dissolved

constituents apparent in the supernatant. However in the samples collected for chemical analysis and left standing for a few days, the water seemed to develop a slight haze which resulted from the precipitation of very fine particles.

By extrapolation of these curves, it can be seen that the TDS levels will not likely exceed 3500 mg/l and the level of specific conductance will remain below 3500 micromhos/cm.

In the tests with fly ash from J. Clark Keith Generating Station (Windsor), specific conductance was the only analysis performed on the supernatant after each mixing. Specific conductance is a measure of the water's capacity to carry an electrical current. It is related to the total concentration of the ionized constituents in a sample of water. It is also a quick method to determine the increase in the TDS after each mixing with the fly ash. The data from the tests were plotted and are shown in Figure 4.

The shape of the curve shows that there is no apparent effect of "levelling off" in the specific conductance or the TDS content even after 10 mixings. As will be discussed later, this condition was probably due to the accumulation of sulphate ions in an acidic solution.

TABLE 2

CHEMICAL ANALYSIS OF FILTERED RECIRCULATION WATER

(Tests with Fly Ash from Lakeview Generating Station)

ANALYSIS*	Control	1	2	3
Aluminum	-	3.3	-	-
Boron	0.07	-	41	39
Calcium	42	810	784	1040
Chloride	34	-	77	46
Cobalt	-	0.6	-	-
Dissolved Solids	180	4800	6980	5720
Iron	-	0.05	-	-
Magnesium	2	23	210	39
pH	7.3	9.5	6.4	9.4
Phosphorus	-	0.03	-	-
Potassium	-	5.2	-	-
Silica	0.64	1.6	60	0.35
Sodium	-	91	-	-
Sp. Cond. @ 25°C	340	4950	6000	5400
Sulphate	27	2500	3380	2250

Sample 1.	After mixing with 7 portions of fly ash
Sample 2.	After mixing with 12 portions of fly ash
Sample 3.	After mixing with 8 portions of fly ash in water heated to 35 - 40°C.

* All analyses except pH and specific conductance are reported in mg/l

TABLE 3

CHEMICAL ANALYSIS OF FILTERED RECIRCULATION WATER

(Tests with Fly Ash from Lambton Generation Station)

ANALYSIS*	Control	1	2
Boron	0.07	11	20
Calcium	38	544	640
Chloride	35	37	46
Dissolved Solids	178	2450	3300
Magnesium	2	14	34
pH	7.4	8.4	8.4
Sp. Cond. @ 25^{o}C	320	2400	3050
Silica	-	1.6	22
Sulphate	27	1480	1490

Sample 1. After mixing with 5 portions of fly ash

Sample 2. After mixed with 14 portions of fly ash

* All analyses except pH and specific conductance are reported in mg/l

TABLE 4

CHEMICAL ANALYSIS OF FILTERED RECIRCULATION WATER

(With Fly Ash from J. Clark Keith Generating Station - Windsor)

ANALYSIS*	1	2	2A
Boron	9.06	9.51	10.1
Calcium	640	600	560
Dissolved Solids	7060	11,300	9500
Magnesium	168	420	460
pH	4.00	4.20	4.20
Spec. Cond. @ 25 ^{o}C	6350	8950	9150
Silica	-	-	-
Sulphates	3400	6200	6300

Sample 1.	After mixing with 5 portions of fly ash.
Sample 2.	After mixing with 10 portions of fly ash.
Sample 2A	This was allowed to stand overnight (16 hr.) and all of the precipitated solids were filtered before analysis.

* All analyses except pH and specific conductance are reported in mg/l

Chemical Analysis of Recirculation Water

The results of chemical analysis performed on the samples of recirculating water are summarized in Table 2 to 4. These samples were collected from each series of tests with the fly ash.

The chemical data show that the calcium and sulphate ions constitute a major portion of the dissolved materials leached from the fly ash by the water. High levels of TDS were extracted from the Windsor sample. It is noted that there was an unusually high concentration of sulphates yielded by the Windsor sample despite the absence of any corresponding increase in the levels of calcium. The water from the Windsor sample was acidic with pH 4.2 in comparison with pH 9.5 in the Lakeview sample and pH 8.4 in the Lambton sample.

Other chemical constituents released in significant quantities were boron, magnesium and silica. Relatively high concentrations of magnesium were found in the samples of recirculating water collected from the Lakeview and Windsor samples. Significant quantities of silica were found in the Lakeview and Lambton samples. Analysis for silica for Windsor are not available. However the data in Table 1 show that silica constitutes a major fraction of the fly ash.

Chemical analyses reveal that appreciable amounts of boron were released by all three samples of fly ash. Boron up to 40 mg/l was found in the recirculating water obtained from Lakeview fly ash while the water from Lambton and Windsor samples yielded 10 to 20 mg/l.

Boron in drinking water is not regarded as a hazard to humans. It is not harmful to fish except at excessively high concentrations as many of the species can survive in waters containing boric acid well over 2000 mg/l without experiencing any extreme difficulties.*

* McKee, J.E. and Wolf, H.W.
WATER QUALITY CRITERIA
2nd Edition State Water Quality Control Board
California Publication No. 3-A (1963)

Boron is an essential element in the nutrition of higher plants yet it is well known that irrigation waters containing amounts in excess of 0.4 to 0.5 mg/l may have deleterious effects on crops. Some of the less sensitive plant crops can tolerate levels of 2 to 4 mg/l boron. In trace quantities, it is known to stimulate the growth of certain species of algae.* For this reason, it may be necessary to examine the effects of boron on algae blooms if the amounts of boron discharged with the recirculating water are significant.

* Lewin, R.A.
PHYSIOLOGY AND BIOCHEMISTRY OF ALGAE
Academic Press, New York P.279 (1962)

Summary and Conclusions:

Laboratory tests were conducted on samples of fly ash obtained from Ontario Hydro's three coal-fired generating stations to determine the extent of dissolved solids that can be expected to build up in the recirculating water if utilized for slurrying and removing the fly ash from the precipitators. In order to obtain simulated samples of recirculating water, a given volume of tap water was used to form a slurry and mixed vigorously with several batches of fresh fly ash in succession.

From these tests it is concluded that:

1. There appears to be an upper limit at which the concentration of TDS will begin to level off in the recirculating water with each sample of fly ash. With the Lakeview fly ash, TDS seemed to level off at 7000 mg/l after recycling with 11 batches of fly ash. With the Lambton fly ash the build up did not increase beyond 4000 mg/l after 14 batches. With the Windsor sample, the level of the TDS reached almost 10,000 mg/l after 10 batches.

2. After recycling several times, the TDS increased in concentration to the point of supersaturation, exceeding the solubility limits of some calcium salts. This causes unstable conditions in the recirculating water resulting in the precipitation of some of the chemical components. This phenomenon would tend to establish an upper limit for the TDS.

3. Highest levels of TDS were noted in the recirculating water in the tests with the fly ash from J. Clark Keith generating station. It had the highest level of sulphates. It was also found to be acidic (pH 4.2).

4. A major portion of the white precipitate formed in the samples of recirculating water from all of the tests appeared to be calcium sulphate.

5. The dissolved materials were leached out more rapidly in water at high temperatures but the resulting solution seemed to be unstable as it was more susceptible to precipitation.

6. Boron was one of the chemical constituents released by all three samples of fly ash. Although it is not considered hazardous to humans and fish, its ultimate effects on algae growths and the chemical quality of the receiving waters should be studied.